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A Guide to BFB Tuning for VOC Analysis

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Introduction

All US EPA methods for volatile organic compounds (VOCs) require that specific GCMS tuning criteria be met before running a calibration curve or analyzing actual samples. The GCMS is tuned using the traditional tuning compound, PFTBA (perfluorotributylamine), and the tune is evaluated every 12 hours by injecting BFB (4-bromofluorobenzene) and measuring the relative intensity of key mass fragments. The MS tuning procedures adjust PFTBA ion responses to achieve the desired BFB response ratios. The relative ion abundance of the BFB mass fragments must meet specific criteria established in the methods to ensure that the GCMS instrument operating conditions are adjusted and optimized for analysis of VOCs, and the criteria must be met every 12 hours to guarantee that the instrument performance remains stable enough for continued analysis.

This poster describes tuning conditions for the Shimadzu GCMS-QP2010 SE (Figure 1) developed to meet the BFB relative abundance criteria described in US EPA methods for analysis of VOCs.

Figure 1: Shimadzu GCMS-QP2010 SE

Tuning Criteria

The BFB tuning criteria for the most common US EPA VOC methods are very similar, although there are a few notable differences. Table 1 compares the BFB Relative Abundance Criteria for five different US EPA VOC methods.

Table 1: Comparison of BFB Relative Abundance Criteria for US EPA VOC Methods

	Relative Abundance Criteria				
Mass (m/z)	Method 524.2	Method 524.3	Method 624	Method 8260C	CLP-SOW
50	15 to 40% of 95	NA	15 to 40% of 95	15 to 40% of 95	15 to 40% of 95
75	30 to 80% of 95	NA	30 to 60% of 95	30 to 60% of 95	30 to 80% of 95
95	Base Peak, 100%	Base Peak, 100%	Base Peak, 100%	Base Peak, 100%	Base Peak, 100%
96	5 to 9% of 95	5 to 9% of 95	5 to 9% of 95	5 to 9% of 95	5 to 9% of 95
173	<2% of 174	<2% of 174	<2% of 174	<2% of 174	<2% of 174
174	>50% of 95	>50% of 95	>50% of 95	>50% of 95	50 to 120% of 95
175	5 to 9% of 174	5 to 9% of 174	5 to 9% of 174	5 to 9% of 174	4 to 9% of 174
176	>95 to <101% of 174	>95 to < 105% of 174	>95 to <101% of 174	>95 to <101% of 174	95 to 101% of 174
177	5 to 9% of 176	5 to 10% of 176	5 to 9% of 176	5 to 9% of 176	5 to 9% of 176

Experimental

Tune Conditions

The factory default tune settings are designed to provide a generalized tune which can be used for a variety of applications. The default tune algorithm adjusts source and lens voltages so that PFTBA ion abundances meet predetermined target abundances, and optimize sensitivity across a wide mass range (Figure 2A).

When tuning for VOC methods, the tune conditions are modified to change the PFTBA target abundances so a subsequent analysis of BFB will meet the relative abundance criteria established in the methods. Figure 2B shows the tune conditions recommended for BFB tuning on the Shimadzu GCMS-QP2010 SE.

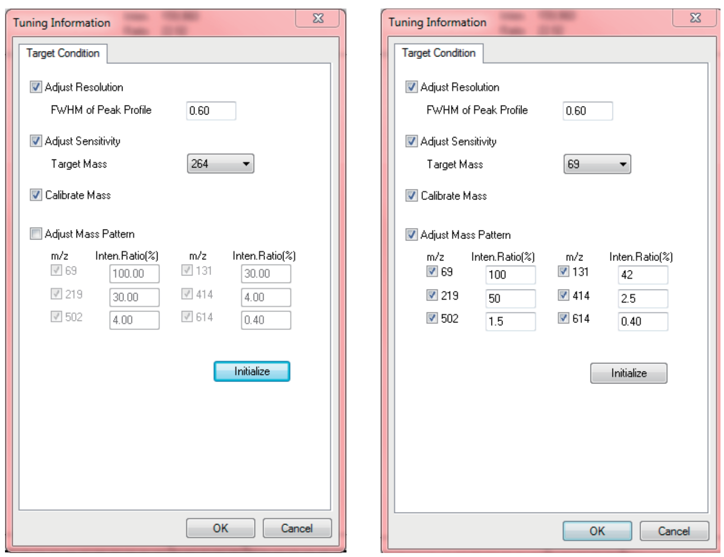

Figure 2A (left): General Purpose Default Tune Conditions

Figure 2B (right): Recommended BFB Tune Conditions Using *m/z* 69 as the Target Mass and Mass Pattern Adjustment

These conditions were found to produce a tune that met the strict BFB relative abundance criteria for all VOC methods on multiple instruments, and remained stable over the evaluation period of approximately 3 months (Table 2).

Table 2: Typical Results from BFB Tune Evaluation Using US EPA Method 624 Method Criteria

Mass (m/z)	Relative Abundance Criteria	Result	Status
50	15 to 40% of 95	16.3	*Pass*
75	30 to 60% of 95	43	*Pass*
95	Base Peak, 100%	100	*Pass*
96	5 to 9% of 95	5.5	*Pass*
173	< 2% of 174	1.4	*Pass*
174	> 50% of 95	63.4	*Pass*
175	5 to 9% of 174	7.1	*Pass*
176	> 95% but < 101% of 174	97.2	*Pass*
177	5 to 9% of 176	6.3	*Pass*

Results and Discussion

Stage One

The first stage of this study was a detailed analysis of the individual GCMS and instrument tune parameters, to find the optimized tune conditions that would consistently meet the BFB relative abundance criteria and produce reliable, stable results. This stage covered a 7-week period, during which 16 individual sequences were run assessing a variety of different instrument and tune variables. The Internal Standard (IS) and Surrogate Standards (SS) were monitored to evaluate stability; results are summarized in Table 3.

Table 3: Summary of Method 524.2 IS and SS Stability, Run as 16 Sequences Over 7 Weeks during Stage One of the Study

Summary of Method 524.2 Stability Results				
Sequence Number	Sequence Details	IS Area Count %RSD	SS#1 Area Count %RSD	SS#2 Area Count %RSD
1	Run 7/28/2014, n = 32	2.90%	2.50%	2.80%
2	Run 7/30/2014, n = 35	6.50%	4.10%	4.60%
3	Run 7/31/2014, n = 33	3.90%	3.00%	4.40%
4	Run 8/8/2014, n = 34	2.40%	2.90%	3.00%
5	Run 8/11/2014, n = 32	4.00%	2.10%	1.90%
6	Run 8/12/2014, n = 35	2.10%	2.60%	2.60%
7	Run 8/14/2014, n = 30	5.30%	9.40%	5.20%
8	Run 8/15/2014, n = 30	3.30%	5.40%	5.10%
9	Run 8/18/2014, n = 33	2.20%	3.20%	1.90%
10	Run 8/19/2014, n = 35	3.90%	5.70%	4.40%
11	Run 8/20/2014, n = 40	5.40%	7.60%	6.80%
12	Run 8/22/2014, n = 33	1.80%	4.10%	2.80%
13	Run 9/2/2014, n = 34	5.30%	4.20%	4.60%
14	Run 9/3/2014, n = 35	8.50%	8.10%	4.30%
15	Run 9/4/2014, n = 31	5.30%	8.00%	5.30%
16	Run 9/8/2014, n = 15	1.90%	3.30%	3.30%
IS = Fluorobenzene				
SS#1 = 4-Bromofluorobenzene				
SS#2 = 1,2-Dichlorobenzene-d4				

Stage Two

Using a single tune file over approximately 2½ months, multiple sequences were run to evaluate BFB performance and IS and SS stability, followed by a complete validation study for US EPA Method 624. As required by the method, at the beginning of each 12-hour period an aliquot of BFB was purged and analyzed, and the relative abundance of mass peaks were evaluated against the criteria set out in the method. The 12-hour BFB tune evaluation samples passed all method criteria in virtually every case over the 2½ month period, using a single tune file. The instrument did not require re-tuning during the evaluation period. The BFB relative abundance criteria for 15 sequences over 2½ months are shown in Figure 3.

Figure 3: Evaluation of BFB Tune Criteria for 15 Sequences Run Over a 2½ Month Period. The Instrument Did Not Require Re-Tuning, and the Same Tune File Was Used During the Entire Period.

Internal Standard Stability

Seven of the sequences were run over a period of four weeks to complete a validation study for US EPA Method 624vii. Each sequence was comprised of 21 to 32 individual sample analyses. The IS area counts for all 197 analyses are plotted in Figure 4.

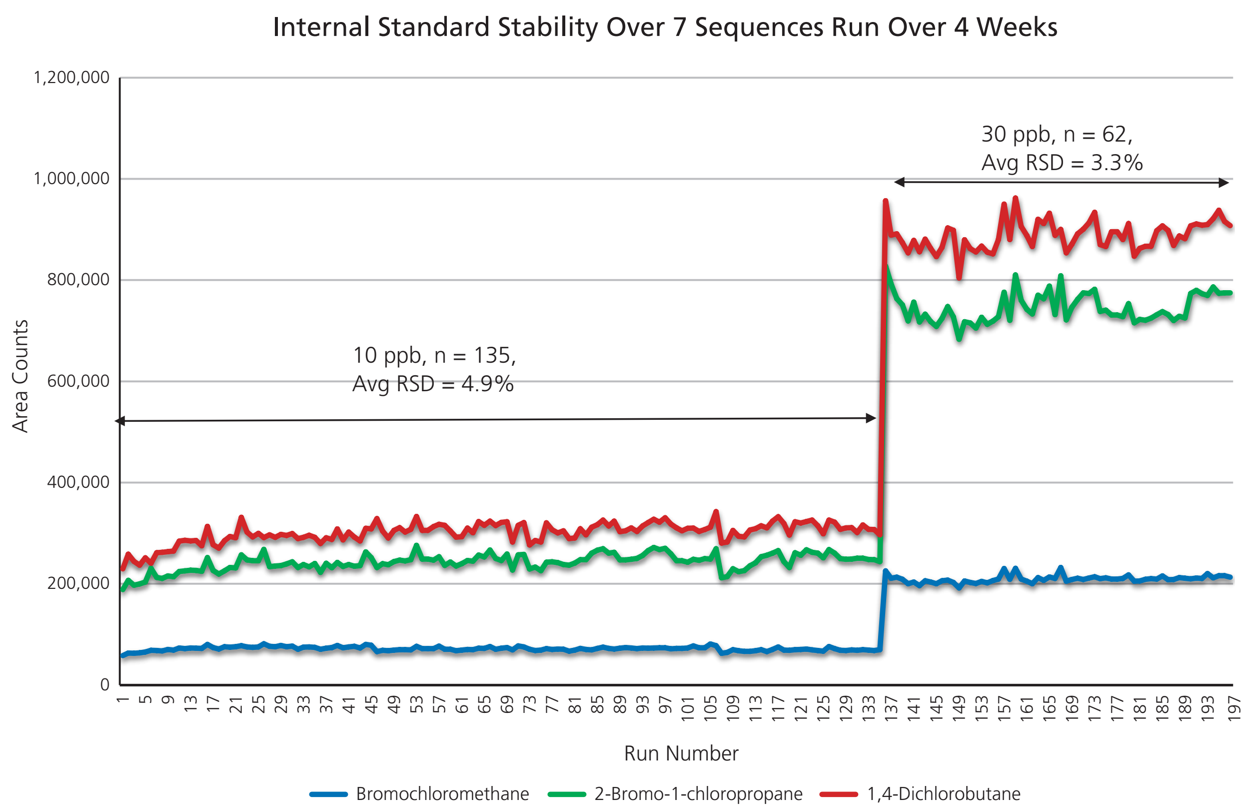

Figure 4: US EPA Method 624 Internal Standard Stability for 7 Sequences (197 Analyses) Run Over 4 Weeks

Summary and Conclusions

The recommended tune conditions shown here easily meet all BFB Tune Evaluation criteria defined in all US EPA methods for analysis of Volatile Organic Compounds by GCMS. A single tune file produced BFB data that met the criteria for all sequences run over at least three months.

During the evaluation period, a validation study for US EPA Method 624 met all defined method criteria, producing stable IS and SS peak areas and passing BFB Tune Evaluations. The instrument did not require re-tuning at any time during the validation study.

References

1. Shimadzu Guide to BFB Tuning for Analysis of Volatile Organic Compounds, GCMS Application News No. GCMS-1405.
2. Shimadzu Guide to US EPA Method 624 for Analysis of Volatile Organic Compounds in Wastewater, GCMS Application News No. GCMS-1406.
3. Method 524.3, Measurement of Purgeable Organic Compounds in Water by Capillary Column Gas Chromatography/Mass Spectrometry, Version 1.0 June 2009, EPA Document #EPA 815-B-09-009.
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5. Method 8260C, Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS), Revision 3, August 2006.

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